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14. Abstract

This work sought to develop chemical components and self-assembly techniques for molecular electronic circuits. Specific objectives were to use membrane replication methods to make segmented metal and semiconductor rod colloids, and to develop techniques for assembling them into cross-point arrays for functional circuits. The major accomplishments were demonstration of nanowire synthesis down to diameters of 12 nm with aspect ratios exceeding 100, development of an electrofluidic technique for aligning and measuring the electronic conductivity of individual wires, and development of chemical control over the assembly of nanowires. The latter involved orthogonal self-assembly of molecules onto electrochemically defined "stripes" along the wire length. Using DNA base pairing, suitably striped wires could be assembled into cross- and T-junctions, and onto lithographically defined patterns on surfaces. Methods were developed for layer-by-layer growth of concentric shells of insulators and conducting polymers on the nanowire walls. This allows the crossing of insulated wires without shorts and crossing of functionalized wires for memory or logic function. Fluidic techniques were developed for making 2-D arrays of nanowires assemble into ordered rafts in microwells. Together these advances provide potentially useful materials and techniques for the realization of very dense (more than 10 billion devices per square centimeter) self-assembled electronic circuits.

Inorganic Self-Assembly Routes to Three-Dimensional Memories and Logical Mesostructures

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Technical Objectives:

This work sought to develop chemical components and self-assembly techniques for molecular electronic circuits. As silicon technology approaches fundamental physical limits, radical changes in devices and circuit architectures will be needed to continue current trends in miniaturization and increased speed. Our goals were to develop a toolbox of functional building blocks (nanoscale segmented metal rods, nanoscale diodes, molecular switches, and DNA linkers) and self-assembly rules that would allow us to construct addressable and configurable cross-point logic circuits and memories. Because chemical assembly techniques are subject to the rules of thermodynamics and therefore produce defective structures, the focus of our theoretical and circuit design efforts was on defect-tolerant circuits that do not require deterministic placement of wires and logic/memory bits. Long-term objectives included the assembly of dense cross-point nanoblock "fabrics," with two-dimensional densities in the 10^11-10^12/cm^2 range, and three-dimensional colloidal crystal memories with capacities in the terabit range. The same assembly techniques are potentially useful for other microelectronic and photonic applications, such as photonic bandgap crystals, that utilize building blocks with dimensions in the range of tens to hundreds of nanometers.

Our specific objectives under this grant were to use membrane replication methods to make segmented metal and semiconductor rod colloids, and to develop techniques for assembling them into cross-point arrays for functional circuits. Some of the basic scientific questions were how one controls the assembly of non-spherical colloidal objects using non-covalent interactions,

electrofluidics, and microlfuidics, how one can incorporate active elements (such as memory bits or diodes) into crossed-wire arrays, how contacts and address lines can be integrated with self-assembled function blocks, how entire circuits and wafers can be aligned and stacked using chemical self-assembly methods, and how different architechtures and error correction schemes mitigate the effects of defects and non-deterministic placement of components.

Technical Approach:

Our approach to this problem involved a combination of chemical synthesis and assembly, microelectronic fabrication and measurement, and theoretical modeling of architectures.

On the chemical side, the objectives were (1) to develop techniques for making monodisperse collections of cylindrical rods with diameters in the 10-200 nm range and lengths in the range of microns; (2) to prepare segmented rods, which contain a definite sequence of metal and/or semiconductor "stripes;" (3) to develop chemical derivitization techniques, which selectively attach molecules to certain stripes; (4) to develop synthetic routes to molecular and nanoparticle-based memory bits; (5) to control the interactions of functionalized rods with each other, with memory bits, and with complementary patterns on silicon substrates, in order to assemble small "function blocks" that act as logic gates or memory elements; and (6) to make self-assembing interconnects and logic restoration circuits for crossed-wire programmable gate arrays.

Impact/Navy Relevance:

Microelectronic devices are pervasive in advanced technologies used by the Navy. This research was driven by the basic need for faster electronics and higher capacity memory devices. It is anticipated that traditional microelectronic fabrication techniques will soon reach the end of the road of miniaturization, and that chemical techniques for fabricating devices from the "bottom up," combined with engineering methods that work from the "top down" will be needed. This project sought to develop materials and methods that will enable the implementation of these technologies within the next decade. Dense terabit memory blocks have a large variety of important uses in communication, targeting and image processing electronics in both defensive and offensive roles. They provide enormous storage capacity for their size, and at present cannot be built with standard technology. The methods we are developing will likely be an important part of electronic fabrication in the near future, and so crucial to all electronically oriented parts of Navy programs.

Progress:

The goal of our work was to develop chemical assembly routes to ultra-high density memory and logic devices. This work involved an interdisciplinary team of chemists, engineers, and physicists. Our near-term target was to develop a synthetic route to crossbar arrays of metallic nanowires with memory bits or electronic switches at the crossing points, at a density that is unattainable within the current or anticipated manufacturing limits of microlithograpy. Our most important successes were as follows:

(1) We extended the electrochemical synthesis of high aspect ratio nanowires down to 12 nm diameter, which provides a building block for crossbar arrays at unprecedented density (10^11 devices per centimeter.

(2) We made "striped" metal nano-rods from metallic, semiconducting, and molecular components. For example, we made metal-semiconductor-metal and metal-molecule-metal wires that act as diodes. In the latter the rectifying molecular junction between metal surfaces is only one molecule thick. We

incorporated negative differential resistance (NDR) molecules into these structures, which await testing at low temperature.

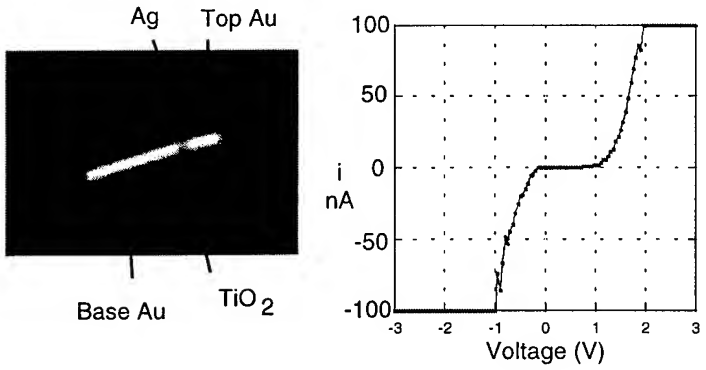


Figure 1. Optical micrograph and I-V curve of a 200-nm dia. nanoparticle diode. The i-V curve was obtained by electrofluidic alignment of a nanowire into a test circuit.

(3) We refined our electric field alignment methods to make individual crosses from nanowires. For convenience in imaging the crosses, most of this work was done with 70-200 nm diameter wires, but we will soon extend it to smaller diameters.

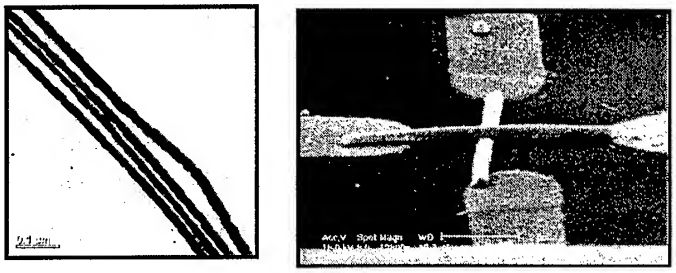


Figure 2. 15-nm diameter Au wires, and a 200-nm diameter nanowire cross made by electrofluidic assembly.

(4) The thermodynamics of self-assembly of single-stranded DNA on nanowires was studied, and this information has been used to optimize the hybridization to complementary sequences for linking wires to surfaces and to other wires. Our DNA linking methods for nanowires were improved to the point where we can obtain high coverages of wires on appropriately patterned surfaces, as well as dimer and trimer nanowire structures such as crosses, T's, and triangles. This work is now being extended to the synthesis of "deterministic" rod bundles in which particular stripe patterns are joined side by side in a definite sequence. This work is a prelude to making crossbar function blocks of DNA-lined wires by fluidic and electrofluidic alignment.

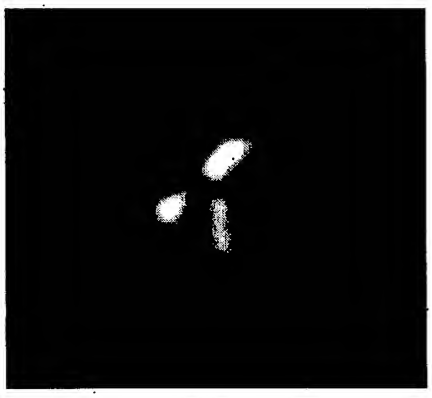


Figure 3. Left: scanning electron micrographs of crossed 70-nm diameter Au/Pt/Au rods; right: optical micrograph of a 200-nm diameter DNA-assembled "T". Crosses and T's were prepared in solution by hybridization of DNA on their middle segments and ends with a linking oligonucleotide. A control experiment in which a noncomplementary linking oligo was used did yield some crosses and T's, but a smaller number.

(5) We developed methods for layer-by-layer growth of concentric shells of insulators and conducting polymers on the nanowire walls. The method leaves the tips of the wires exposed. This technique allows us to cross insulated wires without shorts, to cross functionalized wires for memory or logic function, and to connect the tips of the wires to other circuit elements by electroless metal plating.

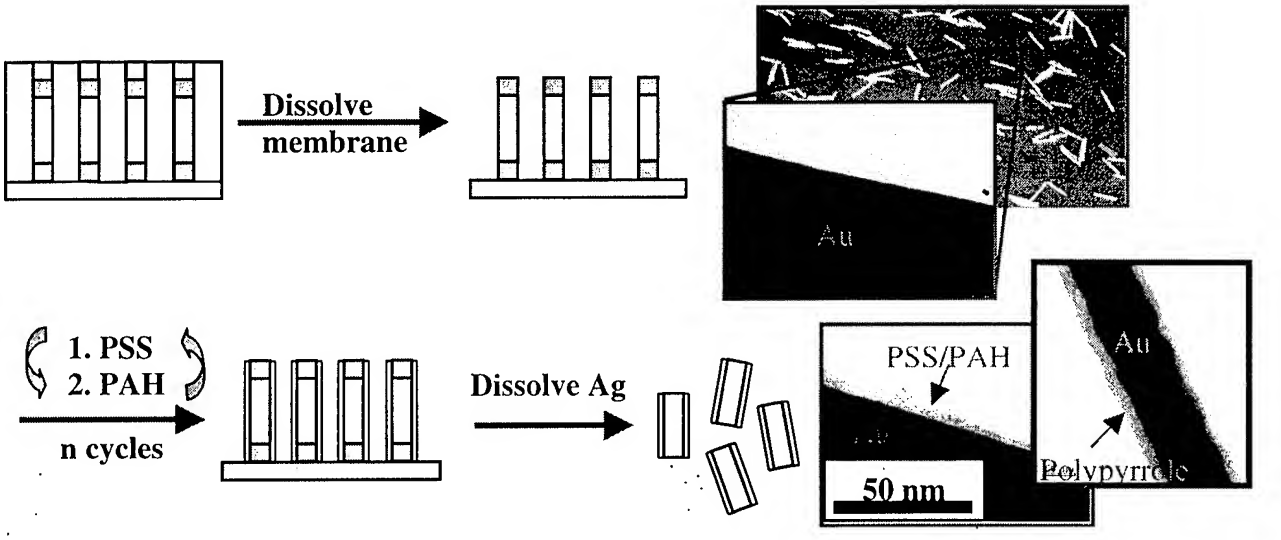
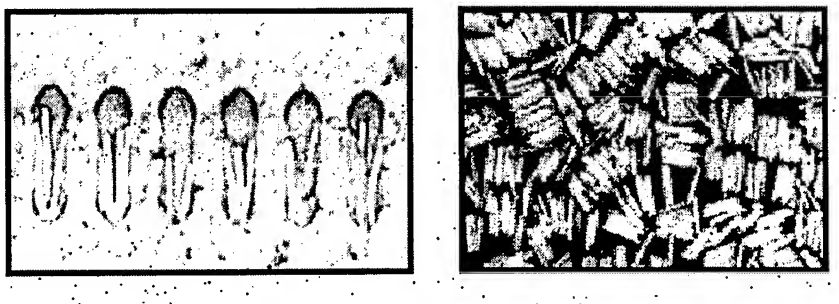


Figure 4. Layer-by-layer derivatization of nanowire walls. Sequential adsorption of 1 nm-thick layers of poly(styrenesulfonate), PSS, and poly(allylamine hydrochloride), PAH, 10 cycles, gives the insulating film shown in the TEM image at the bottom of the figure. A similar technique is used to coat a 70 nm diameter Au wire with a 10 nm-thick poly(pyrrole) film, as shown at the lower right. The tips of the wires are exposed by dissolution of the sacrificial Ag layer. Experiments with fluorescently labeled thiols show that the tips of the nanowires (but not the insulated walls) are reactive with SAM-forming molecules.

(6) We developed fluidic methods for aligning bundles of nanowires in shallow depressions (made photolithographically) on surfaces. The goal here was to define lithographically a function block that is filled with functional elements (wires, switches, logic gates...) of sublithographic size. The shape and size of the lithographically defined well determines the number and orientation of nanowires that align in the well. For proof of concept, we used a "squeegee" to control the flow of underivatized nanowires. We are currently studying surface modifying layers that direct the wires to assemble into smectic bundles, and are experimenting with microfluidic flows directed by patterned polydimethylsiloxane (PDMS) stamps.

Figure 5. Filling of relief patterns with underivatized 200 nm Au nanowires using the "squeegee" method (left). Polymer coated Au nanowires



self-assemble into smectic bundles at a liquid-liquid interface (right).

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D. J. Pena, B. Razavi, P. A. Smith, M. J. Natan, T. S. Mayer, T. E. Mallouk, and C. D. Keating, "Electrochemical Synthesis of Multi-Material Nanowires as Building Blocks for Functional Nanostructures," MRS Symp. Proc., submitted.

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Christine D. Keating, "High Aspect Ratio, Segmented Metal Nanoparticles for Bioassays and Nanoscale Electronics", oral presentation at ELECTROCHEM'2000, Dublin City University, Dublin, Ireland, September 13, 2000.

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Invention Disclosures and Patent Applications

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Michael J. Natan, Thomas E. Mallouk, Benjamin R. Martin, Brian D. Reiss, Louis J. Dietz, and James L. Winkler, "Method of Manufacture of Colloidal Rod Particles as Nanobar Codes," U.S. Patent Application 09/677,203, filed October, 2000.

T. N. Jackson and T. S. Mayer, "Self Assembly of Nano, Micro, and Macro Structures for Microelectronic and Microelectromechanical Systems, U. S. Serial No. 09/608,796, PSU Invention Disclosure 99-2138, filed June 29, 2000.

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T. N. Jackson, "Lateral Nanostructure by Vertical Processing," PSU Invention Disclosure

T. N. Jackson, "Electrolyte-Assisted Molecular Devices," PSU Invention Disclosure

T. N. Jackson, "Improved Contacts for Molecular Devices," PSU Invention Disclosure

Honors/Awards/Prizes

Christine Keating accepted a tenure track position as an Assistant Professor of Chemistry at Penn State University.

Brian Reiss was awarded a MRS Gold student award at the Fall 2000 Materials Research Society Meeting.

Theresa Mayer was awarded the 2000 Penn State Engineering Society Outstanding Teacher Award

Graduate Students

Brian D. Reiss, Ph.D., Chemistry, August 2001 (Natan/Keating)
David J. Peña, Ph.D., Chemistry (Natan/Keating)
Christopher Baiocco, M.S., Electrical Engineering, August 2001, (Jackson)
Baharak Razavi – M.S., Electrical Engineering, (Jackson)
Karthik Shankar – M.S., Electrical Engineering, (Jackson)
Lili Jia – Ph.D. Engineering Science (Jackson)
Chung-Chen Kuo – Ph.D., Electrical Engineering (Jackson)
Benjamin R. Martin, Ph.D., Chemistry (Mallouk)
Sarah St. Angelo, Ph.D., Chemistry (Mallouk)
Donna Furnanage, M.S., Electrical Engineering, December 2000 (Mayer)
Peter A. Smith, M.S., Electrical Engineering, August 2001 (Mayer)
James Matzella, Ph.D., Intercollege Materials Program (Mayer)
Marco Cabassi, Ph.D., Electrical Engineering (Mayer)
Christopher Nordquist, Ph.D., Electrical Engineering, 25% DARPA (Mayer)
Adam J. Rondinone, Ph.D., Chemistry (Zhang)

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Nina I. Kovtyukhova, Chemistry (Mallouk)
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Ludmil Zambov, Electrical Engineering (Mayer)

Female graduate students: 3
Female postdoctoral associates: 3
Minority graduate students: 1
Minority postdoctoral associates: 1
Asian graduate students: 2
Asian postdoctoral associates: 0